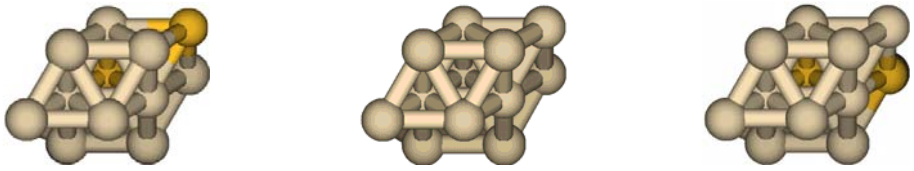
Supporting Information

PtOs Surface Segregation Study: Periodic DFT Calculations using the Seqquest Code

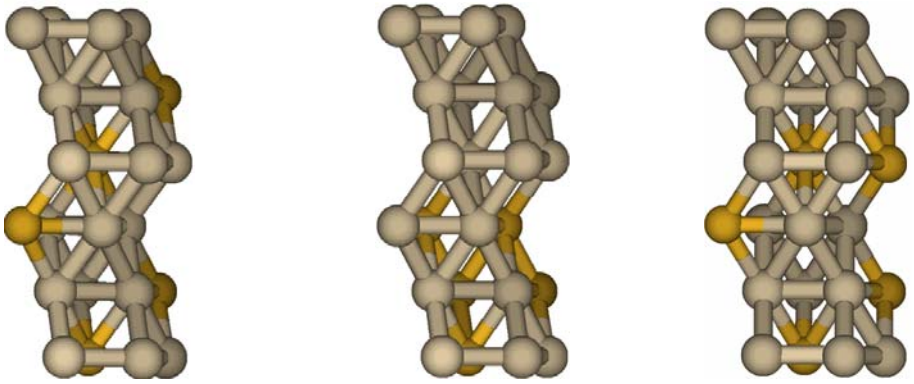
A 6 layer 2x2 periodic model:

A 6 layer 2x2 cell slab contains 5 Os atoms and 19 Pt atoms, which makes the Os:Pt ratio close to 5/24 ≈0.21. The top layer is pure Pt in all structures. The *a* structure contains 5 Os atoms uniformly disctributed in 5 lower layers. The *b* structure has 3 top layers of pure Pt, the 4th and 5th layers consist of 50% Os and 50% Pt, and the bottom layer contains 25% Os and 75% Pt. The *c* structure has 2 top layers of Pt, the 3rd layer is built from 50% Os and 50% Pt, and each of the bottom three layers consist 25% Os and 75% Pt. The most stable structure is *b* with three layers of Pt on the top followed by the *c* structure with two layer of Pt on the top. The energies in the Figure are relative to the energy of the most stable *b* structure, −58503.53 eV.

Top view



Side view



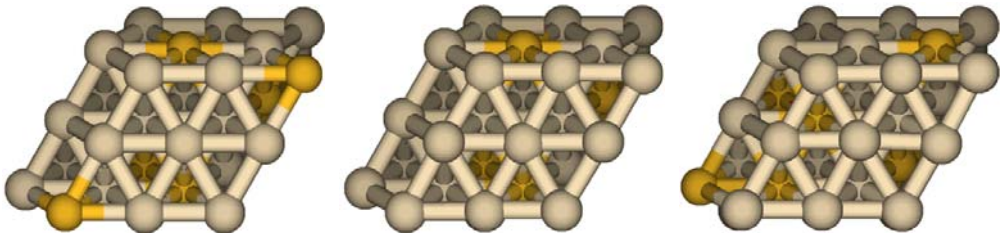
1.69 eV **0 eV** **0.98 eV**

a ***b*** ***c***

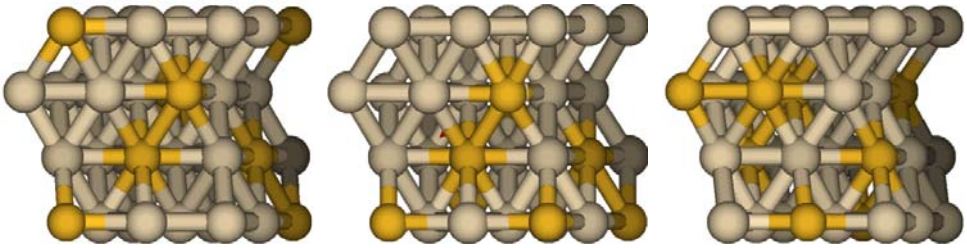
A 4 layer 3x3 periodic model:

A 4 layer 3x3 cell slab contains 8 Os atoms and 28 Pt atoms, which makes the Os:Pt ratio equal to 8/36=0.20. In the *a* structure, the Os atoms are uniformly distributed among the four layers, two Os atoms in each layer. The *b* structure has pure Pt at the top layer, two Os atoms in the second and third layer, and four Os atoms in the bottom layer. The most stable *c* structure is consists of pure Pt at the surface, four Os atoms in the second layer (the Os:Pt ratio is 4/9≈0.45), and two Os atoms in each of the following layers. This segregated structure is similar to the most stable structure obtained for the Pt_3Os alloy [51] which shows strong surface segregation: 100% Pt at the top surface layer, 50% Pt in the second layer, and 75% Pt in each of the following layers. The energies in the Figure are relative to the energy of the most stable *c* structure, –87456.92 eV.

Top view



Side view



1.68 eV **1.79 eV** **0 eV**

a ***b*** ***c***

Theoretical Lattice Parameter of Pt_2Os

The crystal structure of Pt-Os alloy is a face-centered cubic (FCC), which has two distinct lattice sites; the corner site and the face-center site. To estimate the lattice parameter of Pt_3Os, we position the Pt atom at the face-center site and the Os atom at the corner site. This arrangement represents the chemical makeup of Pt_3Os. However, if we want to calculate the lattice constant of Pt_2Os, we could not use the simple FCC unit cell because the addition of Os atoms at any specific face-center site is expected to alter the bonding direction and strength. As a result, the unit cell of Pt_2Os would not be a cubic system. In addition, it is rather difficult to construct a bigger super lattice like 3×3×3 cell and estimate the theoretical lattice parameter of Pt_2Os because it is very challenging and inaccurate to distribute the Os atoms at different sites which could make Pt_2Os as a greater $L1_2$ cubic structure cell.

For Pt_3Os system, we have calculated the lattice vectors which are based on the three-dimensional Pt_3Os FCC lattice constant. Subsequently, we have used the optimized Pt_3Os lattice constant to construct the DA-Pt_2Os(~Pt_4Os) slabs for segregation calculation. We adopt the $L1_2$ cubic structure with Pt atoms at the center of the faces and Os atoms at the corners. The reciprocal space grid is 12×12×12. The optimized lattice constant is 3.94 Å, which is slightly smaller than 3.98 Å obtained from a pure Pt lattice. To compare with experimental results, we also synthesize Pt_3Os and Pt_4Os (alloyed nanoparticles) using identical reflux approach. From the XRD patterns (shown below), a gradual shift of Pt (111) diffraction peaks to lower angles was taking place with increasing Pt content in the PtOs alloyed nanoparticles. The estimated lattice constants of Pt/C (Pt nanoparticles supported on XC-72 from BASF), Pt_2Os/C, DA-Pt_2Os, Pt_3Os, and Pt_4Os are 3.95, 3.81, 3.85, 3.87, 3.88 Å, respectively. In the literature, it is understood that the lattice parameter of a nanoparticle contracts with decreasing nanoparticle sizes ***[R1]***. Hence, it is anticipated that the XRD-estimated lattice parameters of the as-synthesized samples become smaller than what are predicted from the theoretical calculation. Comparisons of lattice parameters from Pt_3Os and Pt in both theoretical and experimental results show a contraction less than 2%.

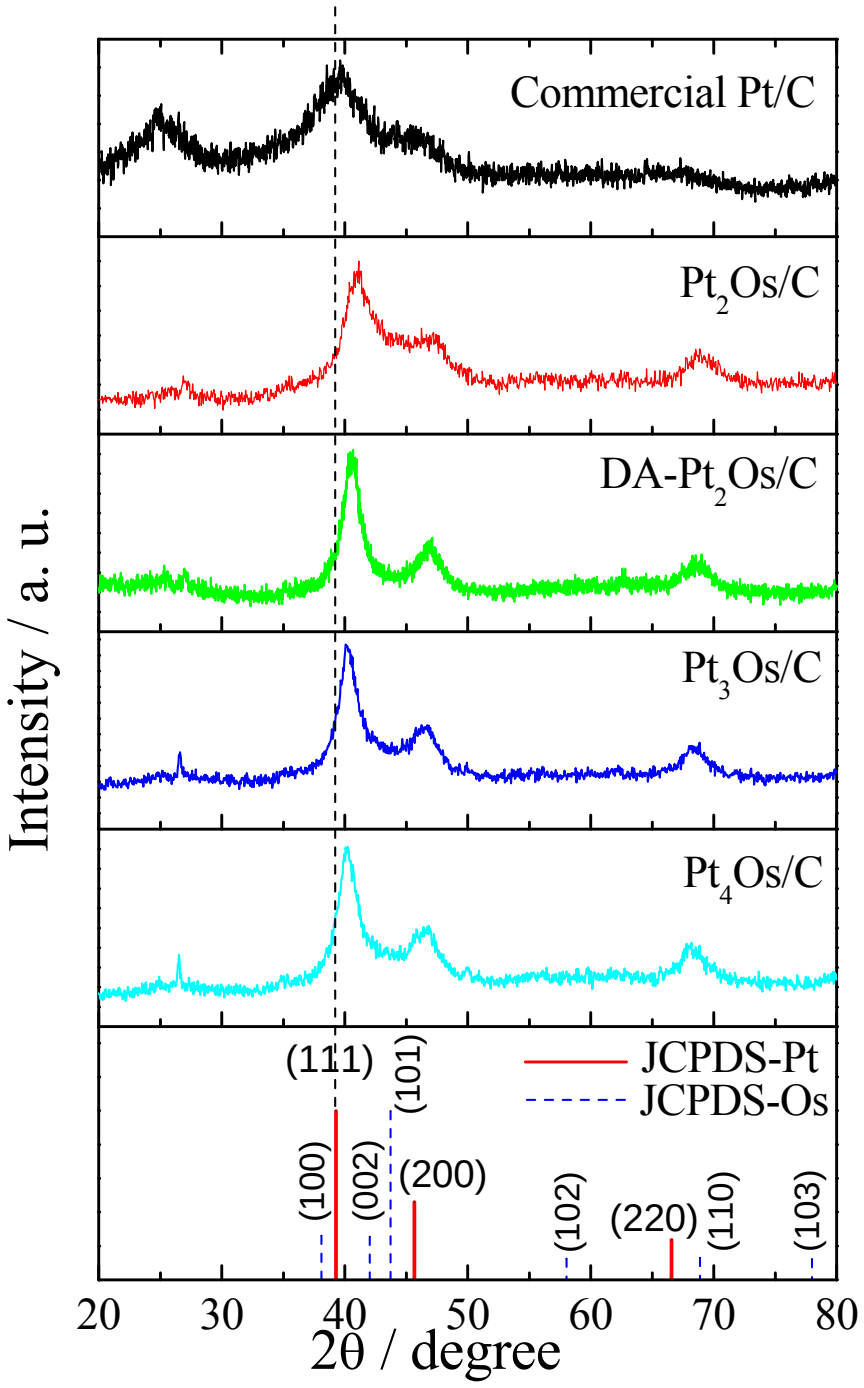


Fig. S1: *The XRD patterns of Pt/C, Pt_2Os, DA-Pt_2Os, Pt_3Os, and Pt_4Os. The standard Pt and Os are JCPDS #88-2343 and #88-1704, respectively.*

[R1]: *Qi et al., "Size effect on the lattice parameters of nanoparticles", Journal of Materials Science Letters, 21 (2002) 877-878.*

Determination of Nanoparticle Sizes from TEM Images

The nanoparticle sizes of Pt/C, Pt_2Os, and DA-Pt_2Os are determined by TEM images using an image processing software known as ImageJ. The counted nanoparticles for Pt/C, Pt_2Os, and DA-Pt_2Os are 150, 333, and 101, and their average sizes are 2.58, 3.55, and 3.86 nm, respectively.

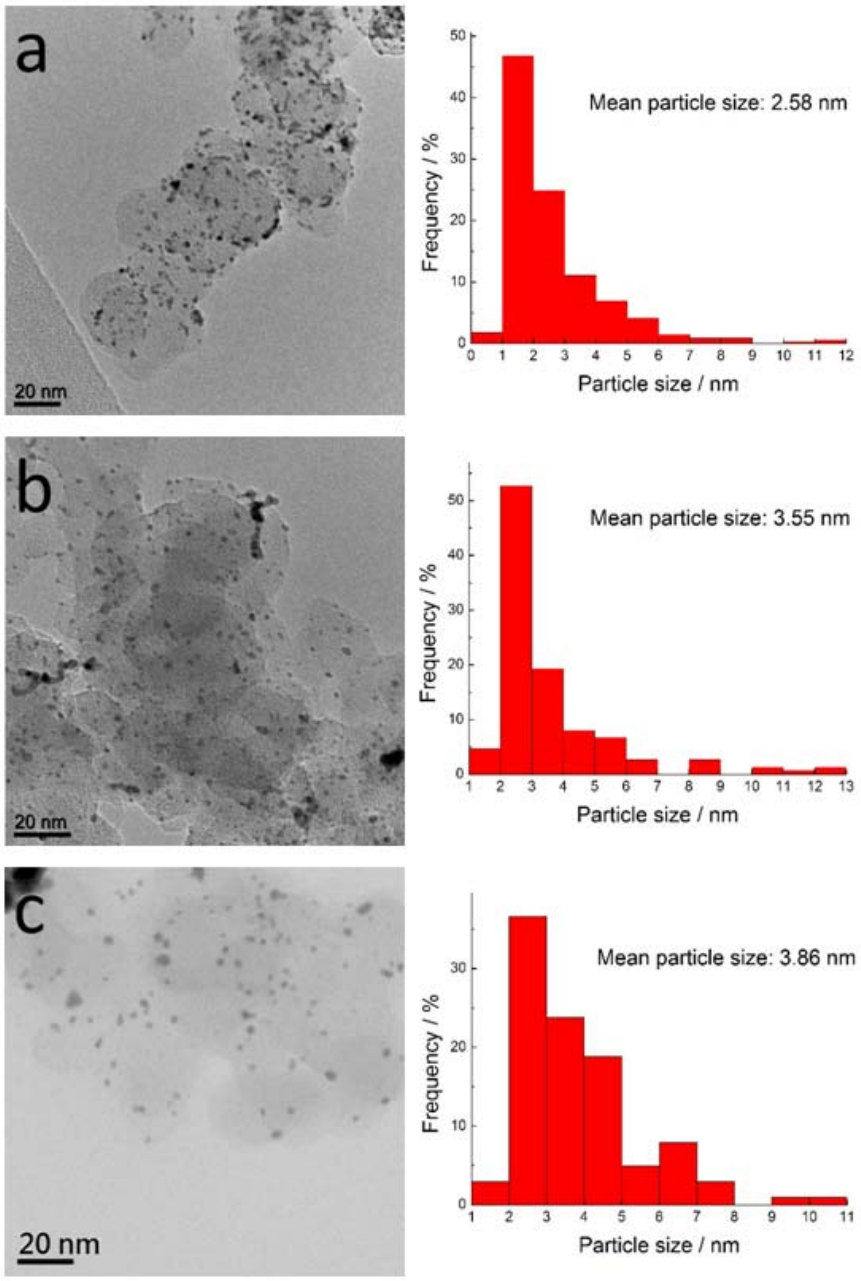


Fig. S2: *The TEM images and size distributions for (a) Pt/C, (b) Pt_2Os/C, and (c) DA-Pt_2Os/C.*